STRESS RELAXATION IN HIGH POLYMERS

By

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The prediction of dynamic energy losses from stress relaxation data, using the equation

\[ \eta = \frac{\eta_0}{4.606} \left( \text{slope of stress relaxation curve} \right) \]

has received considerable attention recently, but for polyisobutylene the correlation between predicted and experimental values of energy loss has been poor. This lack of agreement may have been caused by the failure of the simple "step" distribution function of relaxation times to explain the process adequately. In this work, stress relaxation measurements with the RCA 5734 electronic transducer tube have been made in polyisobutylene at times as early as .01 second and the results show a very rapid rise in stress as \( t \to 0 \) rather than the constant value required by the "step" function.

Another distribution function may be obtained by measuring the slopes of the log. dynamic modulus vs. log. \( \omega \), and the static modulus vs. log. time curves. For PIB the absence of data in the region near 1 second leaves a gap of nearly 2 cycles of log. time for which there are no predicted values of the distribution function and the data obtained in this research may be used to fill this gap. Simplified calculations with this function show qualitative agreement between predicted and experimental energy loss in polyisobutylene.

Dynamic data for Acetate rayon show an increase in energy loss with increased humidity, and stress relaxation experiments were performed on this material at various humidities to see if the effect was apparent. From equation (1) an increase in slope of the relaxation curve is expected to occur as the
humidity is increased. No indication of this effect was found in the stress relaxation data, and in fact, the relaxation curves at higher humidity had slightly lower slopes. This would tend to indicate that the prediction of energy loss from equation (1) is not valid in the case of Acetate rayon.

Values of energy loss for Viscose rayon and Egg Albumin fiber at 65% humidity show moderate agreement with those calculated from stress relaxation experiments.
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INTRODUCTION

In recent years, a considerable amount of work has been done on the mechanical properties of high polymers, under both static and dynamic conditions. Various stress-strain-time measurements are commonly made, for example, creep under constant load\(^1\), stress relaxation at constant elongation\(^1\) and energy loss during harmonic vibration\(^2\). This thesis will be concerned chiefly with stress relaxation, the experiment in which the variation of stress with time at constant strain is observed.

With the types of apparatus commonly used, few stress relaxation measurements are taken before several seconds have elapsed after extension of the sample\(^{13,15,16,17}\). Further, dynamic readings are seldom made at vibration frequencies below one cycle per second, a frequency which corresponds approximately to one second on the stress relaxation time scale. This leaves a gap over which no mechanical data are available and it is the object of this work to make stress relaxation measurements in the region of very short times after straining the sample, corresponding to vibrational frequencies greater than one cycle per second.

High polymers are unique in that they are able to undergo large deformations under stress, the deformations being reversible to varying degrees. Two effects are apparent when a polymer is deformed. The first is the completely elastic part which conforms to Hooke's Law and the second, the irreversible part, may follow Newton's viscosity relation, such that the rate of extension varies as the stress, or may follow some more complicated non-Newtonian viscosity relation\(^4\).

The simplest experiment to illustrate these effects is the so-called "creep" experiment in which a load is attached to one
end of a filament, the other end being fixed, and the extension is measured as a function of time (figure 1). The initial extension measures the completely reversible part, while that which occurs as time proceeds measures irreversible viscous flow. Sometimes a third mechanism occurs, a retarded elastic effect, such that part of the delayed extension is recovered. In other words, if a sample has been undergoing creep and the load is suddenly released, the extension will suddenly decrease because of the instantaneous elastic mechanism, and further decrease will occur as time proceeds, caused by the retarded elastic contribution. Full recovery will not be obtained, however, because of the irreversible flow mechanism.

Mechanical properties are generally described in terms of mechanical models consisting of arrangements of springs and dashpots to represent elastic deformation and irreversible flow respectively. The simplest arrangement is perhaps the Maxwell Model consisting of one spring and one dashpot in series (figure 2). If the unit is stretched by a fraction of its original length $\varepsilon$ and the extension thereafter held constant, the stress will decay logarithmically, governed by the equation $S = S_0 e^{-t/\tau}$, where the rate constant $\frac{1}{\tau}$ is equal to $\frac{E}{\eta}^{5.6}$. This type of experiment, in which decay of stress is observed at constant strain, is called a stress relaxation experiment.
The Maxwell unit might be used to explain creep also but it has been found more convenient to employ the Voigt unit (figure 3) for this purpose. Similarly, the Three-element Model (figure 4) is more convenient for explaining some "dynamic" effects, as for example, the variation of stress with strain at constant rate of elongation or of loading, and the stress-strain relationships in some vibrational experiments.

The use of a single Maxwell unit leads to a stress relaxation curve like that shown in Figure 5. The theoretical curve may be compared with experimental curves for Hevea gum stock (natural rubber) and polyisobutylene. It may be seen that while the natural rubber produces a stress relaxation curve which corresponds closely to the theoretical curve, the curve for polyisobutylene decays at a much slower rate. To fit curves for substances which do not follow the theoretical curve, a number of Maxwell units, each with different $\tau$, may be connected in parallel and, in the case of polyisobutylene, every stress relaxation curve may be fitted by using the appropriate distribution.
Fig. 5. Stress relaxation curves for Hevea Gum stock and polyisobutylene, shown with the predicted relaxation for a single Maxwell unit.

\[
E(\tau) = \begin{cases} 
\frac{E^o}{\tau}, & (\tau_e < \tau < \tau_m) \\
0, & (\tau < \tau_e, \ \tau > \tau_m)
\end{cases}
\]

Fig. 6. Parallel array of Maxwell units with "step" distribution function.
of relaxation times (values). One very simple distribution to which curves for polyisobutylene have been fitted assumes an infinite parallel array of Maxwell units (figure 6) such that the number of units with relaxation times between \( \tau \) and \( \tau + d\tau \) is 

\[ N(\tau)\,d\tau \]

The modulus associated with these units is \( E(\tau)d\tau \); the total "instantaneous" modulus being 

\[ E = \int_0^\infty E(\tau)d\tau \]

The particular distribution function \( E(\tau) \) chosen by Andrews, Hofman-Bang and Tobolsky is a "step" distribution which has a constant value between two limits (figure 6). It is easily shown that the value \( E^* \) may be obtained from the slope of the straight-line portion of the stress relaxation curve. This function fits stress relaxation data for polyisobutylene fairly well at the long-time end but predicts a plateau at the short-time end beginning from \( t_0 \) and extending toward \( t = 0 \).

Another distribution of relaxation times, of which the above is a simplification, is that obtained by determining the slope at each point along the stress relaxation curve and plotting the negative slope against \( \log \tau \). This distribution may be extended to shorter \( \tau \) values by considering dynamic data.

The actual molecular mechanisms involved in the processes of elastic deformation and flow have not been completely worked out and, indeed, vary with the type of polymer. For example, polysulfide rubbers undergo stress relaxation in accordance with the simple exponential function 

\[ S = S_0 e^{-\frac{t}{\tau}} \]

indicating that a single type of bond is responsible for the relaxation, while other polymers require a distribution of \( \tau \) values to explain the effect. Relaxation in polysulfide rubbers has been found to be due to oxidative scission along the molecular chain, for when the relaxation is performed in highly purified nitrogen the relaxation rate is
The highly elastic deformation occurring in rubber-like high polymers is certainly due to uncoiling of polymer segments from a random orientation between two juncature points to a more ordered one under the action of the stress. Upon release of the tension the segments may go back to their initial random orientation, the process being completely reversible. The loss of "randomness" is associated with an entropy change and the process is sometimes referred to as entropy elasticity. The flow mechanism, which is the irreversible part of the relaxation, must involve rearrangement of the molecules as a whole with respect to each other. This may be caused by rupture of primary bonds or secondary interactions between molecules or by slippage of whole molecules impeded by an internal friction.

Stress relaxation measurements have been made with a wide variety of polymers\(^8,10,13,15,17\) and the general characteristics of the stress relaxation curve have been well established. Polyisobutylene has received a great deal of attention in this respect \(^7,8,10,18,19\) since it is non-polar and since it has a very simple structure, being believed to be completely linear. Tobolsky and Brown\(^10\) have made an intensive study of the elastoviscous properties of polyisobutylene showing the effect of molecular weight, temperature and elongation. They found that the shape of the stress relaxation curve (stress/elongation vs. log time) was independent of temperature and elongation, and that a change in temperature served only to move the curve along the time axis. They also found that activation energies for the stress relaxation process were essentially constant from 30-100° C. but that at lower temperatures, especially at -35°C. and lower the
stress magnitudes increase greatly and curves become non-superimposable. At room temperature, then, we would expect a great increase in the stress which we might observe at very short times after the initial strain, which is the time origin for the stress relaxation experiment. Such an expectation is based on the qualitative equivalence between cooling the sample and observing stress values at shorter times in a stress relaxation experiment.

When a visco-elastic material is subjected to a sinusoidal stress \( S = S_o \cos(\omega t) \), the material responds with a sinusoidal variation in strain \( \varepsilon = \varepsilon_o \cos(\omega t) \). In the apparatus used by Dunell and Dillon\(^2\), a coil to which fibers are attached at each end is suspended between the poles of a magnet and voltage from a low frequency oscillator is applied to the coil. The current passing through the coil is a measure of the stress applied to the system and the maximum elongation \( \varepsilon_o \) is measured by cathetometer.

The dynamic properties of a material may be described by a Voigt unit (figure 3) in which the parameters \( \eta \) and \( E \) are frequency-dependent. The motion of the system under sinusoidal force\(^2\) \( f = f_o \cos(\omega t) \) is given by:

\[
M \frac{d^2x}{dt^2} + \frac{2A}{\ell} \eta \frac{dx}{dt} + \frac{2A}{\ell} E x = f_o \cos(\omega t)
\]

where \( x \) is the displacement of the vibrator unit, \( t \) is the time, \( M \) the mass vibrating, \( \omega \) the radian frequency, \( A \) the cross-sectional area of the fiber and \( \ell \) the length of each of the two fibers.

Equation (1) is solved for \( x \), and from the data at mechanical resonance --- the condition where \( x_{\max}/f_{\max} \) is maximum with frequency --- \( E \) and \( \eta \) can be calculated\(^2\). The assumptions are made that \( \eta \omega \) and \( E \) are constant with change in frequency.
The value $\eta^2$ is proportional to the energy loss per cycle per unit volume of material and may be called the hysteresis index.

It has been found possible to predict the value of $\eta^2$ from stress relaxation data. Using the "step" distribution of relaxation times (figure 6) the value of $\eta^2$ is given by $\frac{\pi E^o}{2}$ where $2.303 E^o$ is the slope of the stress relaxation curve.

Dynamic experiments with Acetate Rayon show an increase in energy loss ($\eta^2$) with increased humidity. As a check of the formula $\eta^2 = \frac{\pi E^o}{2}$, stress relaxation experiments were performed on Acetate Rayon.
EXPERIMENTAL METHOD

Many types of apparatus with which to measure stress relaxation are described in the literature. The majority of these, adapt the beam or platform balance to this use but other types use calibrated metal springs, kymographs, and piezoelectric crystals. One method measures the resonance frequency of lateral vibrations in a stretched sample to obtain stress measurement.

When it is considered that measurements as early as 0.01 second after extension of the fiber must be made, it becomes apparent that most of the methods listed above cannot be used because of high inertia. However, special transducers with very low inertia are available, for example, the mechano-electronic transducer tube RCA 5734. It was decided to investigate the usefulness of this vacuum tube in stress measurement.

The RCA 5734 (Plates Ia, Ib) is a small triode measuring an inch in length and 3/8 inch in diameter. It is constructed of metal such that there is at one end a diaphragm through which a very thin rod of metal protrudes by 1/8 inch. This rod serves as anode and when a force is applied to the external end of the rod, the diaphragm bends slightly so that the interior part of the anode is moved relative to the cathode, resulting in a change in current through the tube. This change can then be used as a measure of the force applied to the protruding end of the rod. A maximum load of 20 grams can be applied at the end of the rod and at this load the current is changed by roughly 20% from that at zero load. The sensitivity of the tube was found to drop as the tube aged, but this is probably due to excess loads which were inadvertently applied.
PLATE I

(a) RCA 5734 tube.

(b) Tube and clamp.

(c) Distorted Square Wave.

(d) True Square Wave.
Various circuits were tried in order to arrive at the best method of interpreting the signal from the tube, though it was decided from the start that a cathode ray oscilloscope would be the only suitable instrument for recording the short-time relaxation. At longer times, however, the oscilloscope would be rather inconvenient because of drift, and a way of measuring the long-time relaxation had to be devised. As illustrated in figure 7, one possible method was to insert a milliammeter in the plate lead to record the plate current variation. This method was unsuitable since the change in current was small in comparison with the normal current. The similar objection of insufficiency in the change of the position of the trace on the oscilloscope with change in stress also rendered this method unfeasible.

Next, the circuit of figure 8 was tried. Here, the high D.C. voltage occurring at the anode is biased to that with the tube in an unstrained condition, the point A is at zero volts. In addition, a vacuum-tube voltmeter was connected in parallel with the oscilloscope to measure the long-time relaxation. This circuit is valid only because the very high input resistance of both the oscilloscope (2.2 Megohms) and the voltmeter (10 Megohms) allow only an infinitesimal current in the plate take-off lead. The instruments used were a Sylvania Model 132 oscilloscope and a Hickok Vacuum-tube Voltmeter. Both were rather unsatisfactory in that the CRO needed an external DC linear amplifier and also had a non-linear sweep while the VTVM drifted badly. A DuMont Model 304 CRO and a Heath VTVM were then obtained. These were both found to be entirely satisfactory.

A Wheatstone Bridge circuit was considered but since the circuit described in the previous paragraph was more direct in
Figure 7. First experimental circuit.

Figure 8. Second experimental circuit.

Figure 9. Third experimental circuit.

Figure 10. Final experimental circuit.
application it was adopted in preference to the Bridge.

On testing the circuit with a square-wave generator, it was found that distortion occurred at short times (Plate Ic). The trouble was eventually located and found to be caused by capacitance in the bias batteries. The effect interfered only with readings up to about 1/2 second, that is, on those obtained from the CRO. It was considered that if the CRO were attached directly to the tube plate through a high-capacity condenser the trouble might be eliminated. The time constant for the circuit —— time for the voltage to drop to a fraction 1/e of its initial value —— might be adjusted to a value greater than a minute so that the condenser is charged very little in the initial second and during that time acts as an ordinary conductor. In figure 9, consider a voltage to appear suddenly at the plate of the tube; the condenser will charge in accordance with the well-known equation \( V_c = V_0 \left(1 - e^{-\frac{t}{RC}}\right) \). If \( CR \) is large enough, the voltage drop across the condenser during the first second of relaxation will be very small while the remaining voltage will be across the CRO and will appear on the screen. In these experiments, \( CR \) was set at 150, using a 30 mfd 450 V. condenser and a 2.8 Megohm resistor in series with the oscilloscope (2.2 Megohms), at which value the charging during the initial second was about 1 1/2%. The final arrangement is shown in figure 10.

During a run, a 1 1/4 second time exposure photograph of the CRO screen, recording the stress relaxation up to one second, is taken the instant the fiber is stretched. Then at two seconds, a Gra-Lab electric timer energizes the relay (R in figure 10) so that the plate of the 5734 is disconnected from the CRO circuit.
arm and connected to the VTVM circuit arm. Subsequent readings of stress are taken from the VTVM.

Instantaneous stretching of the filament is accomplished by a spring triggered by an electromagnet. The filament clamp (figure 11) is notched to fit an iron bar which holds the clamp against the action of the spring. When the electromagnet is switched on, the iron bar is pulled out of the notch, whereupon the spring stretches the filament.

The plate-supply voltage for the 5734 tube is obtained from a conventional full-wave rectifier, voltage regulated to 300 volts D.C. and fed at 115 volts A.C. from a Sola Constant-Voltage transformer which also supplied both the CRO and VTVM. The rectifier circuit is shown in figure 12.

The apparatus is calibrated by measuring the voltage produced when the 5734 tube is under the tension of the calibrated spring whose length is measured by a cathetometer. The CRO and VTVM are correlated by means of a dry cell and tapping key in the following manner. The circuit shown in figure 13 is inserted at Point B in figure 10 and when the tapping key is depressed, the voltage change which occurs is read from the VTVM. The relay is then switched to the CRO side and the key pressed again. The resulting change in trace height corresponds to the voltage change read from the VTVM. Since the sensitivity of the tube changed as it aged, it was thought advisable to calibrate before each run.

Calculations have been made as to what is the earliest reading which the apparatus may be expected to record reliably. The most important factor involved is the time required for the spring to move the fiber clamp weighing 12.7 grams. The only other variable is the reaction of the tube diaphragm and this has been
Fig. 11. Detail of filament clamp.

Fig. 12. Circuit diagram for power supply.

Fig. 13. Circuit to be inserted when correlating oscilloscope and voltmeter.

Fig. 14. Diagram illustrating parallax error which occurs when CRO is photographed.
calculated from tube data to be less than $10^{-3}$ second. At a spring tension equal to 100 grams and for .1 cm. elongation the response time should be about .005 second and to allow for possible error, no stress readings corresponding to times less than .01 second were plotted from the photographic trace. Values of stress at .01 second are considered to be quite reliable, and indeed, on one run stress was measurable at .005 second. The most convenient method for setting the sweep frequency accurately to establish a time basis for the first part of the experiment, was to set it at 10 sweeps per second and synchronize this with the 60 cycles per second line frequency.

A small parallax error occurs when photographing the face of the GRO tube. This will be apparent from figure 14. A correction curve has been calculated.

For runs at temperatures below room temperature, a cold jacket was constructed. It consisted of a metal box measuring 2 X 2 X 4 inches fitting tightly around the clamp which held the 5734 tube, one side of the box being hinged to form a door and the top being left open. A thick layer of powdered asbestos lagging was applied around the entire exterior. Low temperatures were obtained by bubbling nitrogen through a mixture of dry ice and acetone at such a rate as to obtain the required temperature and then forcing the cool gas into the cold jacket.

In trials with fibrous materials such as rayon, which require regulated humidity, the apparatus was enclosed in a cardboard box and humid air forced into it (Plates IB, IIa). A 65% relative humidity was obtained by bubbling air through a saturated solution of Magnesium Acetate at room temperature.
In this investigation, stress relaxation experiments were performed on 6.6 million molecular weight polyisobutylene (sample W-7-7 of those polyisobutylene samples investigated by Andrews and Tobolsky), 25 denier Acetate and 30 denier Viscose rayons, and on a sample of egg albumin fiber (54% steam elongated). The curves obtained with these materials are shown in Figures 15, 19, 20, 21, 22 and in each case the slopes at both long and short times are indicated. For comparison, the predicted value of energy loss, $\eta \omega$, calculated from the slope of the particular curve and the corresponding value of $\eta \omega$ determined experimentally from dynamic data are shown in Table I.

* Prepared by A.D. MacIntyre in this laboratory.
Figure 15. Stress Relaxation in Polyisobutylene. 24°C. (Sample W-7-7, 6.6 million M. W.)

Figure 16. Composite Curve shown with curves of Tobolsky and Andrews. (Sample W-7-7)
Figure 17. Distribution Function in Polyisobutylene.

Figure 18. Energy loss in Polyisobutylene with points calculated from function in Figure 17.
Figure 19. Stress Relaxation in Acetate Rayon (24°C).

Figure 20. Stress Relaxation in Acetate Rayon (24°C).
Figure 21. Stress relaxation in Viscose rayon (24°C).

Figure 22. Stress relaxation in Egg albumin fiber (24°C).
(a) View of entire apparatus.

(b) Typical trace obtained using polyisobutylene.

(c) Typical trace obtained using rayon.
DISCUSSION OF RESULTS

The results for polyisobutylene (6.6 million M.W.) shown in Figure 15 show a rather poor degree of reproducibility, the extreme high and low values differing by a factor of about 1.5. However, when multiplied by a factor, any curve may be almost exactly superimposed upon another. This suggests that the trouble may lie in the measurement of tension. Clearly, if the point of application of the tension on the protruding end of the transducer tube is altered, the torque applied to the diaphragm will vary, and since strips from a large sheet of polyisobutylene were cut for samples, it is quite probable that variations in thickness would occur. In runs using rayon, which has a more uniform cross-section, the reproducibility was much better. In addition, since all samples were attached to the transducer tube by polystyrene cement, the possibility of having layers of cement of different thicknesses cannot be excluded. The variation in height between the several curves may be attributed almost completely to this difference in torque applied to the tube at given fiber tension, although some sample-to-sample variation may be expected to occur from differences in thickness along the sample. The samples were cut from a sheet of polyisobutylene with a photographic cutter and the cross-sectional area was calculated from the length of the sample, its weight and its density rather than by direct measurement, because the crinkly nature of the surfaces of the original sheet made measurement of the thickness tedious and inaccurate.

Curve (1) in Figure 16 is a composite curve in which each point is the average of the corresponding points on the four experimental curves of Figure 15, and from this composite curve
calculations of slope were taken and comparisons were made with the results obtained from the same sample of material at various temperatures by Andrews and Tobolsky. In the composite curve, the high initial values of stress predicted to occur at very early times are clearly indicated. However, the slopes of the stress relaxation curves obtained in this research are generally slightly higher than those of Andrews and Tobolsky, although the stress values themselves are of similar magnitude. Moderate success is obtained in superimposing the curves for low temperatures (Figure 16) upon the composite curve at early times, although the low temperature curves contain an almost flat portion at times just past those corresponding to the rapid drop in stress while such a plateau is found in only one of the curves obtained here.

Ferry et al. have constructed a graph showing the relaxation distribution function for polyisobutylene calculated from stress relaxation and vibrational data (Figure 17). The curve is necessarily broken because of the absence of data to bridge the gap of nearly two cycles of log time between dynamic data, corresponding to relaxation times less than about a second, and stress relaxation data, corresponding to relaxation times greater than a second. Although the sample used here had molecular weight different from that of the sample used by Ferry, the stress relaxation data obtained here at very early times may be used to calculate the values of the distribution function at times not covered by Ferry's data. The distribution function is obtained by measuring the slope at points along the stress relaxation curve and at times corresponding to the relaxation time desired. For example,
### TABLE I

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>HUMIDITY</th>
<th>SLOPE</th>
<th>CALCULATED $\eta W$</th>
<th>EXPERIMENTAL $\eta W$ (Ref. 20)</th>
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<tr>
<td>ACETATE</td>
<td>38% (1)</td>
<td>7.87 $10^9$</td>
<td>5.37 $10^9$</td>
<td>0.72 $10^9$</td>
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<tr>
<td>RAYON</td>
<td>38% (2)</td>
<td>4.77 &quot;</td>
<td>3.26 &quot;</td>
<td>0.72 &quot;</td>
</tr>
<tr>
<td>24°C.</td>
<td>58%</td>
<td>3.57 &quot;</td>
<td>2.44 &quot;</td>
<td>1.45 &quot;</td>
</tr>
<tr>
<td>24°C.</td>
<td>65%</td>
<td>3.46 &quot;</td>
<td>2.36 &quot;</td>
<td>2.24 &quot;</td>
</tr>
<tr>
<td>24°C.</td>
<td>76%</td>
<td>5.37 &quot;</td>
<td>3.66 &quot;</td>
<td>2.15 &quot;</td>
</tr>
<tr>
<td>24°C.</td>
<td>82%</td>
<td>3.43 &quot;</td>
<td>2.34 &quot;</td>
<td>2.15 &quot;</td>
</tr>
<tr>
<td>VISCOSSE</td>
<td>65%, 24°C</td>
<td>6.86 &quot;</td>
<td>4.68 &quot;</td>
<td>4.8 &quot; *</td>
</tr>
<tr>
<td>RAYON</td>
<td>&quot;</td>
<td>6.12 &quot;</td>
<td>4.17 &quot;</td>
<td>4.8 &quot; *</td>
</tr>
<tr>
<td>EGG ALBUMIN</td>
<td>&quot;</td>
<td>5.5 &quot;</td>
<td>3.7 &quot;</td>
<td>1.2 &quot;</td>
</tr>
<tr>
<td>FIBER 24°C</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POLYISOBUTYLENE</td>
<td></td>
<td></td>
<td></td>
<td>SEE FIGURE 18</td>
</tr>
</tbody>
</table>

**Ref. 8**
if the slope of the stress relaxation curve at \( t = 10 \text{ sec} \) is 
\(-2 \times 10^9 \text{ dynes/cm}^2\) the height of the distribution function corresponding to \( t = 10 \text{ sec} \) is given by

\[
\phi(b) = -\frac{\text{slope}}{2.303} = 8.7 \times 10^8
\]

The values of the function obtained in this way from the composite curve (Figure 16) are shown with Ferry's data in Figure 17. The values of the distribution function obtained through the composite curve for 6.6 million M.W. are higher than those for the 1.2 million M.W. sample used by Ferry, but this is apparently not entirely due to the difference in molecular weight, for when the data obtained by Andrews and Tobolsky\(^3\) for 1.4 million M.W. is used the values for the distribution function are just as high. The reason for this variation is not clear for the results of Andrews and Tobolsky indicate that the slope of the straight-line portion of the stress relaxation curve is nearly independent of molecular weight. Hence, the height of the distribution function over the level portion of the curve should be the same for all molecular weights. Stress relaxation data vary considerably, however, with different observers\(^3,8,26\).

The curve of the relaxation distribution function is observed to pass through a minimum near relaxation times of one second. This is not apparent from previous distribution functions and indicates that the relaxation mechanisms are divided into two broad groups of relaxation times, one with very short relaxation times and another with long ones.

Energy losses in polyisobutylene have been found to increase sharply with frequency\(^8,9\), a fact which cannot be explained if the simple "step" distribution function (Figure 6) is used. With
the function of Figure 17, however, better correlation between theoretical and experimental values of energy loss will probably be obtained. As a preliminary examination, we may use the formula
\[ \eta = \frac{\pi}{4.646} (\text{slope}) \] to calculate energy loss, taking the slope of the stress relaxation curve at times equal to \( \frac{1}{\omega} \). As the slope varies, then, values of energy loss will also vary. While this method is not intended to give results which are very accurate, it will indicate whether the more complex distribution function predicts energy loss values which increase with frequency. A comparison between energy loss values predicted in this way and those determined experimentally is given in Figure 18.

Results with fibrous materials show rather better agreement with theory than results using polyisobutylene do. Stress relaxation curves for Acetate and Viscose rayon and egg albumin fiber are shown in Figures 19-22. Experiments with Acetate rayon were performed at several humidities while the experiments with the other two materials were done at a constant humidity (65%).

Vibrational experiments with Acetate rayon indicate an increase in energy loss with increased humidity, and from the stress relaxation theory of energy losses this effect should show up in a stress relaxation experiment as a more rapid relaxation at higher humidity. However, no indication of this tendency is found in stress relaxation experiments with Acetate rayon (Figures 19,20). Calculated and experimental values are shown for comparison in Table I. At no point along the stress relaxation curves for low humidity is the slope less than that at higher humidity for corresponding time values. This evidence puts the whole theory of prediction of energy loss from stress relaxation slopes in a rather unfavorable light.
The energy loss calculated from stress relaxation data for the egg albumin fiber is larger than the measured value of energy loss by a factor of more than 3 at the lowest value of slope along the curve.

In conclusion, the results of these experiments indicate that while the predicted values of energy loss in polyisobutylene calculated from stress relaxation data compare favorably with experimental values, the values calculated for fibrous materials give rather poor agreement.
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